

Supporting Information for the Manuscript Entitled

Cationic Zinc Enolates as Highly Active Catalysts for Acrylate Polymerization

Logan E. Garner,[†] Hongping Zhu,[†] Mark L. Hlavinka,[‡] John R. Hagadorn,[‡] and
Eugene Y.-X. Chen^{*†}

*Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523-1872, and
Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309-0215*

Materials and Methods. All syntheses and manipulations of air- and moisture-sensitive materials were carried out in flamed Schlenk-type glassware on a dual-manifold Schlenk line, a high-vacuum line, or in an argon or nitrogen-filled glovebox. NMR-scale reactions (typically in a 0.02 mmol scale in ~0.7 mL of an NMR solvent) were conducted in Teflon-valve-sealed J. Young-type NMR tubes. HPLC grade organic solvents were sparged extensively with nitrogen during filling of the solvent reservoir and then dried by passage through activated alumina (for THF, Et₂O, and CH₂Cl₂) followed by passage through Q-5-supported copper catalyst (for toluene and hexanes) stainless steel columns. Toluene-*d*₈ and benzene-*d*₆ were degassed, dried over sodium/potassium alloy, and filtered before use, whereas CDCl₃ and CD₂Cl₂ were degassed and dried over activated Davison 4 Å molecular sieves. NMR spectra were recorded on either a Varian Inova 300 (FT 300 MHz, ¹H; 282 MHz, ¹⁹F) or a Varian Inova 400 spectrometer. Chemical shifts for ¹H were referenced to internal solvent resonances and are reported as parts per million relative to tetramethylsilane, whereas ¹⁹F NMR spectra were referenced to external CFCl₃.

Monomer *n*-butyl acrylate (*n*-BA) was purchased from Acros and purified by first degassing and drying over CaH₂ overnight followed by distillation under reduced pressure. The purified monomer was stored in brown glass bottles over activated Davison 4 Å molecular sieves in a –30 °C freezer inside the glovebox. BHT-H (butylated hydroxytoluene, i.e., 2,6-di-*tert*-butyl-4-methylphenol) was

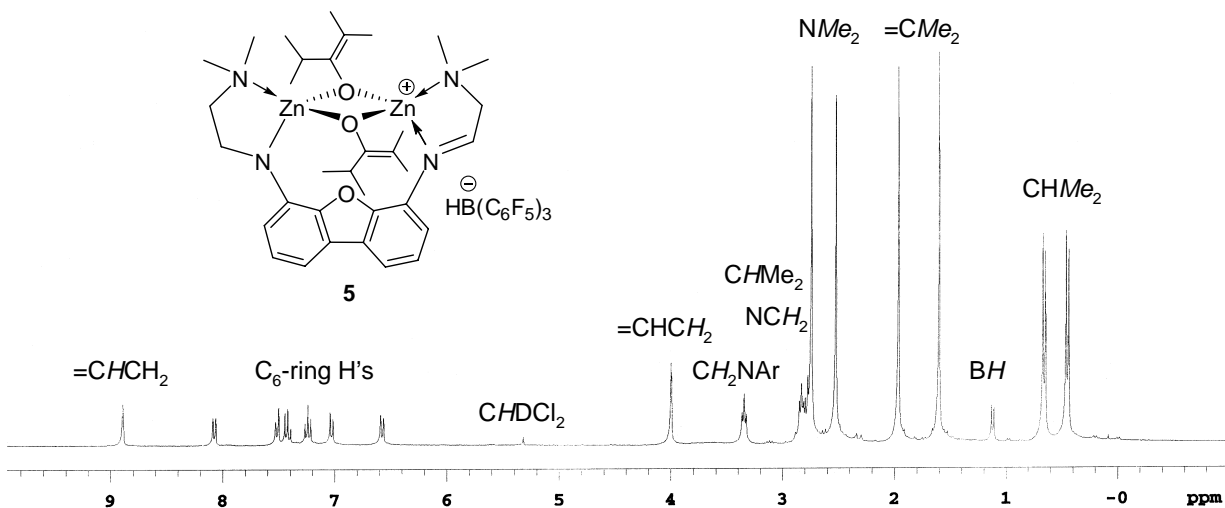
[†] Colorado State University.

[‡] University of Colorado.

purchased from Aldrich Chemical Co. and recrystallized from hexanes prior to use. Tris(pentafluorophenyl)borane $B(C_6F_5)_3$ was obtained as a research gift from Boulder Scientific Co. and further purified by recrystallization from hexanes at $-30\text{ }^{\circ}\text{C}$. Tris(pentafluorophenyl)alane $Al(C_6F_5)_3$, as a 0.5 toluene adduct $Al(C_6F_5)_3 \cdot (C_7H_8)_{0.5}$ based on the elemental analysis for the vacuum-dried sample, was prepared by the ligand exchange reaction of $B(C_6F_5)_3$ and $AlMe_3$ in a 1:3 toluene/hexanes solvent mixture in quantitative yield;¹ this is the modified synthesis based on literature procedures.² *Extra caution should be exercised when handling this material, especially the unsolvated form, because of its thermal and shock sensitivity.*

Zinc enolate complexes $^R\text{LZn}_2[\text{OC}(^i\text{Pr})=\text{CMe}_2]_2$ ($R = \text{Me}$, **1**; $R = ^i\text{Pr}$, **2**) and $^R\text{LZn}_2[\text{OC}(\text{Me}_5\text{C}_6)=\text{CH}_2]_2$ ($R = \text{Me}$, **3**; $R = ^i\text{Pr}$, **4**) were prepared according to literature procedures.³ Cationic zinc enolate complexes **5** and **6** were generated quantitatively by mixing the corresponding neutral precursors **1** and **2** (0.05 mmol scale) with 1 equiv of $B(C_6F_5)_3$ in CH_2Cl_2 (2 mL) at ambient temperature for 10 min in a glovebox; they can be isolated as dark red solids after removal of the solvent. Their stability at ambient temperature is limited to few hours in solid state, and noticeable decomposition can be observed after 10 min in solution, thus making them unsuitable for performing elemental analyses. Nevertheless, they can be readily characterized by solution NMR techniques and low temperature X-ray single-crystal diffraction studies (for complex **5**).

^1H NMR (CD_2Cl_2 , $23\text{ }^{\circ}\text{C}$) for the in-situ generated complex $(^{\text{Me}}\text{L}_\text{H})\text{Zn}_2[\text{OC}(^i\text{Pr})=\text{CMe}_2]_2^+ [\text{HB}(C_6F_5)_3]^-$ (**5**): δ 8.88 (t, $^3J_{\text{HH}} = 4.2\text{ Hz}$, 1H, $=\text{CHCH}_2$), 8.09 (d, $J = 7.5\text{ Hz}$, 1H, Ar), 7.51 (d, $J = 7.5\text{ Hz}$, 1H, Ar), 7.43 (t, $J = 7.5\text{ Hz}$, 1H, Ar), 7.25 (t, $J = 7.5\text{ Hz}$, 1H, Ar), 7.03 (d, $J = 7.5\text{ Hz}$, 1H, Ar), 6.59 (d, $J = 7.8\text{ Hz}$, 1H, Ar), 4.00 (s, br, 2H, $=\text{CHCH}_2$), 3.35 (t, $J = 6.0\text{ Hz}$, 2H, ArNCH_2), 2.83 (t, $J = 6.0\text{ Hz}$, 2H, Me_2NCH_2), 2.81 (sept, $J = 6.8\text{ Hz}$, 2H, CHMe_2), 2.74 (s, 6H, NMe_2), 2.52 (s, 6H, NMe_2), 1.96 (s, 6H, $=\text{CMe}_2$), 1.61 (s, 6H, $=\text{CMe}_2$), 1.12 (d, $^1J_{\text{HB}} = 6.6\text{ Hz}$, 1H, BH), 0.65 (d, $J = 6.9\text{ Hz}$, 6H, CHMe_2), 0.45 (d, $J = 6.9\text{ Hz}$, 6H, CHMe_2). ^{19}F NMR (CD_2Cl_2 , 23°C): δ -132.33 (d, 6F, *o*-F), -162.77 (t, 3F, *p*-F), -165.74 (m, 6F, *m*-F).



^1H NMR (CD_2Cl_2 , 23 °C) for the in-situ generated complex $(^{\text{iPr}}\text{L}_{\text{H}})\text{Zn}_2[\text{OC}(^{\text{iPr}})=\text{CMe}_2]_2^+ [\text{HB}(\text{C}_6\text{F}_5)_3]^-$ (**6**): δ 9.23 (s, br, 1H, $=\text{CHCH}_2$), 8.04 (d, $J = 7.5$ Hz, 1H, Ar), 7.59 (d, $J = 7.5$ Hz, 1H, Ar), 7.41 (t, $J = 7.5$ Hz, 1H, Ar), 7.23 (t, $J = 7.5$ Hz, 1H, Ar), 7.00 (d, $J = 7.5$ Hz, 1H, Ar), 6.54 (d, $J = 7.8$ Hz, 1H, Ar), 4.12 (s, br, 2H, $=\text{CHCH}_2$), 3.57 (sept, $J = 6.8$ Hz, 2H, NCHMe_2), 3.37 (t, $J = 6.0$ Hz, 2H, ArNCH_2), 3.28 (sept, $J = 6.8$ Hz, 2H, NCHMe_2), 3.24 (t, $J = 6.0$ Hz, 2H, Me_2NCH_2), 2.25 (sept, $J = 7.0$ Hz, 2H, CHMe_2), 1.67 (s, 6H, $=\text{CMe}_2$), 1.51 (s, 6H, $=\text{CMe}_2$), 1.29 (d, $J = 6.5$ Hz, 6H, NCHMe_2), 1.21 (d, $J = 6.5$ Hz, 6H, NCHMe_2), 1.11 (br, 1H, BH), 0.57 (d, $J = 6.9$ Hz, 6H, CHMe_2), 0.50 (d, $J = 6.9$ Hz, 6H, CHMe_2). ^{19}F NMR (CD_2Cl_2 , 23°C): δ -132.20 (d, 6F, *o*-F), -162.79 (t, 3F, *p*-F), -165.62 (m, 6F, *m*-F).

General Polymerization Procedures. All polymerizations were carried out in 25 mL or 50 mL Schlenk flasks on a Schlenk line with an external temperature-control bath. In a typical procedure, a zinc complex (6.97 μmol) and the activator $\text{B}(\text{C}_6\text{F}_5)_3$ (6.97 μmol) were loaded into a Schlenk flask followed by addition of 10 mL CH_2Cl_2 . The flask was sealed with a septum, interfaced to a Schlenk line, and placed in a bath at the pre-equilibrated temperature. After the catalyst solution was stirred for 10 min at ambient temperature, a predetermined amount of *n*-butyl acrylate monomer (e.g., for the 1000:1 ratio run, 1 mL, 6.97 mmol) was quickly added via gastight syringe through the septum. After

the desired time interval, a 0.2 mL aliquot was taken and quenched into a 4 mL vial containing 0.6 mL of undried “wet” CDCl₃ stabilized by 250 ppm of BHT-H. The quenched aliquots were analyzed by ¹H NMR to obtain monomer conversion data. Immediately after the aliquot was removed, the polymerization was quenched by addition of 5 mL 5% HCl-acidified methanol. The polymer product was isolated by evaporation of solvent and dried in a vacuum oven at 50 °C to a constant weight. Polymer samples for NMR analysis were further treated by dissolving in benzene followed by filtration and drying.

Polymer Characterizations. Gel permeation chromatography (GPC) analyses of the polymers were carried out at 40 °C at a flow rate of 1.0 mL/min, with CHCl₃ as the eluent, on a Waters University 1500 GPC instrument equipped with four 5 μm PL gel columns (Polymer Laboratories) and calibrated using 10 PMMA standards. Chromatograms were processed with Waters Empower software (version 2002); number-average molecular weight and polydispersity of polymers are given relative to PMMA standards. ¹H NMR (CDCl₃, 23 °C) for poly(*n*-butyl acrylate): δ 4.02 (t, 2H, OCH₂CH₂CH₂CH₃), 2.25 (s, br, 1H, CH₂), 1.88 (s, br, 1H, CH), 1.57 (m, 3H, CH₂ + OCH₂CH₂CH₂CH₃), 1.35 (m, 2H, OCH₂CH₂CH₂CH₃), 0.92 (t, 3H, OCH₂CH₂CH₂CH₃).

Polymerization results by complex **1** at 23 °C were described in the main text, whereas the extended results by complexes **1**, **2**, **3**, and **4** were summarized in Table 1.

X-Ray Crystallographic Analysis of Complex 5. Single crystals of complex **5** suitable for X-ray diffraction were grown from a toluene solution layered with hexanes at –30 °C inside the freezer of a glovebox. The crystals were quickly covered with a layer of Paratone-N oil (Exxon, dried and degassed at 120 °C/10^{–6} Torr for 24 h) after the mother liquors were decanted and then mounted on a thin glass fiber and transferred into the cold nitrogen stream of a Bruker SMART CCD diffractometer. The structure was solved by direct methods and refined using the Bruker SHELXTL program library by full-matrix least-squares on *F*² for all reflections.⁴ All non-hydrogen atoms were located by difference Fourier synthesis and refined anisotropically, except for those solvent toluene carbon atoms

which were refined isotropically. All hydrogen atoms were included in the structure factor calculations at idealized positions, except for H(1) bound to the boron center, which was located by the difference Fourier synthesis and refined isotropically. One toluene solvent molecule was disordered and treated in two parts, and the corresponding occupation was refined as 0.495 and 0.305, respectively. Another toluene solvent molecule was only disclosed by one-half moiety with the occupation of 0.50; owing to the thermal vibration as well as the low occupation, the C–C bond length and C–C–C angle in this molecule were refined with a little deviation to the ideal value, although some fixations were set. These gave rise to several C-level (check and explain) alerts shown on the checkCIF report. Selected crystal data and structural refinement parameters as well as selected bond lengths and angles are collected in Tables 2 and 3.

Table 1. Results of *n*-Butyl Acrylate Polymerizations by Zinc Complexes **1–4**/B(C₆F₅)₃ ^a

entry no.	zinc comp.	[<i>n</i> -BA]/[Zn]	[BAr ₃]/[Zn]	temp (°C)	time (min)	conv. ^b (%)	<i>M</i> _n ^c (kg/mol)	PDI ^c (<i>M</i> _w / <i>M</i> _n)
1	1	200	1	0	10	100	105	2.29
2	1	400	1	0	10	100	197	2.69
3	1	600	1	0	10	100	219	2.79
4	1	800	1	0	10	100	316	2.70
5	1	1000	1	0	60	100	325	2.85
6	2	200	1	23	10	100	69.9	2.66
7	2	400	1	23	10	100	95.6	2.88
8	2	600	1	23	10	100	185	3.16
9	2	800	1	23	10	100	211	3.09
10	2	1000	1	23	10	100	233	3.26
11	3	400	1	23	300	100	79.4	1.97
12	3	1000	1	23	30	29	149	2.64
13	3	1000	1	23	60	61	158	2.69
14	3	1000	1	23	120	85	120	2.64
15	4	400	1	23	300	100	87.3	2.10
16	4	1000	1	23	30	32	159	6.19
17	4	1000	1	23	60	45	171	5.73
18	4	1000	1	23	120	68	150	3.33
19	4	1000	1	23	180	77	144	3.20
20	4	1000	1	23	240	81	126	2.83

^a Carried out in Schlenk flasks on a Schlenk line using an external temperature-control bath and a complex-activation mode (i.e., addition of the bulk *n*-BA to the preformed catalyst solution derived from the premixing of a zinc complex with B(C₆F₅)₃ in 10 mL CH₂Cl₂ for 10 min at indicated temperature. ^b Monomer conversions were determined by ¹H NMR of aliquots. ^c Number-average molecular weight (*M*_n) and polydispersity index (PDI) determined by GPC relative to PMMA standards in CHCl₃.

Table 2. Crystal Data and Structure Refinement for Complex **5**.

Identification code	ec37a
Empirical formula	C _{59.35} H _{60.15} BF ₁₅ N ₄ O ₃ Zn ₂
Formula weight	1304.01
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 14.0040(3) Å alpha = 109.117(2) deg. b = 15.6990(6) Å beta = 113.3840(10) deg. c = 16.6964(4) Å gamma = 98.152(2) deg.
Volume	3023.03(15) Å ³
Z, Calculated density	2, 1.433 Mg/m ³
Absorption coefficient	0.886 mm ⁻¹
F(000)	1337
Crystal size	0.22 x 0.13 x 0.04 mm
Theta range for data collection	1.56 to 33.11 deg.
Limiting indices	-21 ≤ h ≤ 21, -24 ≤ k ≤ 24, -25 ≤ l ≤ 24
Reflections collected /unique	99182 / 22872 [R(int) = 0.1013]
Completeness to theta = 33.11	99.5 %
Absorption correction	SADABS
Max. and min. transmission	0.9620 and 0.8269
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	22872 / 5 / 759
Goodness-of-fit on F ²	1.016
Final R indices [I > 2sigma(I)]	R1 = 0.0655, wR2 = 0.1480
R indices (all data)	R1 = 0.1737, wR2 = 0.1855
Largest diff. peak and hole	1.233 and -0.545 e.Å ⁻³

Table 3. Selected Bond lengths (Å) and angles [deg] for Complex **5**.

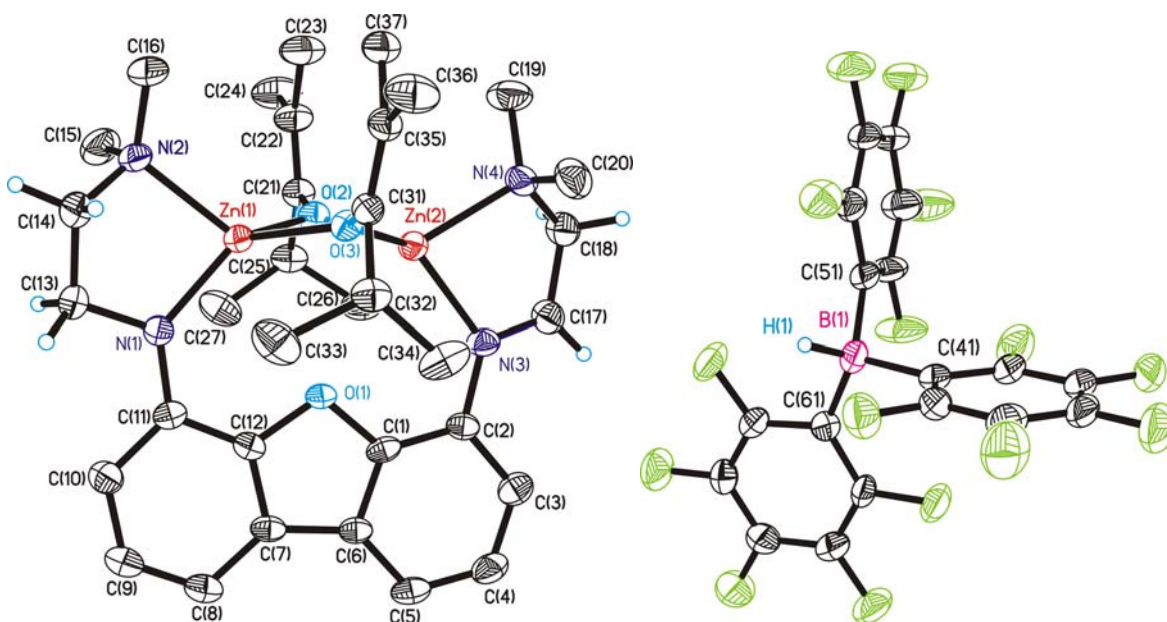
Zn(1)-N(1)	1.937(3)	C(7)-C(12)	1.393(4)
Zn(1)-O(2)	1.971(2)	C(7)-C(8)	1.411(5)
Zn(1)-O(3)	1.991(2)	C(8)-C(9)	1.358(5)
Zn(1)-N(2)	2.078(3)	C(9)-C(10)	1.405(4)
Zn(1)-Zn(2)	2.8484(5)	C(10)-C(11)	1.414(4)
Zn(2)-O(3)	1.930(2)	C(11)-C(12)	1.391(4)
Zn(2)-O(2)	1.943(2)	C(13)-C(14)	1.513(5)
Zn(2)-N(3)	2.036(2)	C(17)-C(18)	1.493(5)
Zn(2)-N(4)	2.068(3)	C(21)-C(22)	1.341(4)
O(1)-C(1)	1.376(3)	C(21)-C(25)	1.506(5)
O(1)-C(12)	1.410(4)	C(22)-C(23)	1.503(5)
O(2)-C(21)	1.406(4)	C(22)-C(24)	1.523(5)
O(3)-C(31)	1.387(4)	C(25)-C(27)	1.526(5)
N(1)-C(11)	1.375(4)	C(25)-C(26)	1.540(5)
N(1)-C(13)	1.434(4)	C(31)-C(35)	1.334(4)
N(2)-C(15)	1.477(4)	C(31)-C(32)	1.513(4)
N(2)-C(16)	1.481(4)	C(32)-C(34)	1.524(5)
N(2)-C(14)	1.482(4)	C(32)-C(33)	1.527(5)
N(3)-C(17)	1.304(4)	C(35)-C(37)	1.509(4)
N(3)-C(2)	1.421(4)	C(35)-C(36)	1.509(5)
N(4)-C(18)	1.480(4)	B(1)-H(1)	1.071(32)
N(4)-C(19)	1.486(4)	B(1)-C(51)	1.631(6)
N(4)-C(20)	1.489(5)	B(1)-C(41)	1.645(5)
C(1)-C(2)	1.385(4)	B(1)-C(61)	1.646(5)
C(1)-C(6)	1.395(4)		
C(2)-C(3)	1.403(4)	N(1)-Zn(1)-O(2)	130.16(10)
C(3)-C(4)	1.383(5)	N(1)-Zn(1)-O(3)	123.56(9)
C(4)-C(5)	1.383(5)	O(2)-Zn(1)-O(3)	81.92(8)
C(5)-C(6)	1.401(4)	N(1)-Zn(1)-N(2)	86.66(11)
C(6)-C(7)	1.437(5)	O(2)-Zn(1)-N(2)	117.75(10)

O(3)-Zn(1)-N(2)	121.46(10)	C(2)-N(3)-Zn(2)	127.3(2)
N(1)-Zn(1)-Zn(2)	129.03(7)	C(18)-N(4)-C(19)	110.6(3)
O(2)-Zn(1)-Zn(2)	42.92(6)	C(18)-N(4)-C(20)	110.0(3)
O(3)-Zn(1)-Zn(2)	42.57(6)	C(19)-N(4)-C(20)	109.1(3)
N(2)-Zn(1)-Zn(2)	144.30(8)	C(18)-N(4)-Zn(2)	104.4(2)
O(3)-Zn(2)-O(2)	84.21(9)	C(19)-N(4)-Zn(2)	115.5(2)
O(3)-Zn(2)-N(3)	131.21(9)	C(20)-N(4)-Zn(2)	107.1(2)
O(2)-Zn(2)-N(3)	122.90(10)	O(1)-C(1)-C(2)	124.6(3)
O(3)-Zn(2)-N(4)	118.97(10)	O(1)-C(1)-C(6)	111.5(3)
O(2)-Zn(2)-N(4)	121.06(10)	C(2)-C(1)-C(6)	124.0(3)
N(3)-Zn(2)-N(4)	83.35(11)	C(1)-C(2)-C(3)	116.0(3)
O(3)-Zn(2)-Zn(1)	44.25(6)	C(1)-C(2)-N(3)	118.9(3)
O(2)-Zn(2)-Zn(1)	43.69(6)	C(3)-C(2)-N(3)	125.1(3)
N(3)-Zn(2)-Zn(1)	130.13(8)	C(4)-C(3)-C(2)	121.3(3)
N(4)-Zn(2)-Zn(1)	146.44(7)	C(5)-C(4)-C(3)	121.6(3)
C(1)-O(1)-C(12)	105.4(2)	C(4)-C(5)-C(6)	118.7(3)
C(21)-O(2)-Zn(2)	134.88(19)	C(1)-C(6)-C(5)	118.5(3)
C(21)-O(2)-Zn(1)	131.68(19)	C(1)-C(6)-C(7)	106.3(3)
Zn(2)-O(2)-Zn(1)	93.39(8)	C(5)-C(6)-C(7)	135.2(3)
C(31)-O(3)-Zn(2)	132.79(18)	C(12)-C(7)-C(8)	118.8(3)
C(31)-O(3)-Zn(1)	134.01(18)	C(12)-C(7)-C(6)	106.1(3)
Zn(2)-O(3)-Zn(1)	93.18(9)	C(8)-C(7)-C(6)	135.1(3)
C(11)-N(1)-C(13)	117.7(3)	C(9)-C(8)-C(7)	117.5(3)
C(11)-N(1)-Zn(1)	129.9(2)	C(8)-C(9)-C(10)	122.7(3)
C(13)-N(1)-Zn(1)	112.3(2)	C(9)-C(10)-C(11)	122.0(3)
C(15)-N(2)-C(16)	109.7(3)	N(1)-C(11)-C(12)	120.8(3)
C(15)-N(2)-C(14)	110.7(3)	N(1)-C(11)-C(10)	126.0(3)
C(16)-N(2)-C(14)	109.3(3)	C(12)-C(11)-C(10)	113.3(3)
C(15)-N(2)-Zn(1)	108.5(2)	C(11)-C(12)-C(7)	125.8(3)
C(16)-N(2)-Zn(1)	118.3(2)	C(11)-C(12)-O(1)	123.5(3)
C(14)-N(2)-Zn(1)	99.94(18)	C(7)-C(12)-O(1)	110.7(3)
C(17)-N(3)-C(2)	121.2(3)	N(1)-C(13)-C(14)	110.2(3)
C(17)-N(3)-Zn(2)	111.2(2)	N(2)-C(14)-C(13)	112.3(3)

N(3)-C(17)-C(18)	118.9(3)	O(3)-C(31)-C(32)	113.8(2)
N(4)-C(18)-C(17)	111.8(3)	C(31)-C(32)-C(34)	111.4(3)
C(22)-C(21)-O(2)	120.1(3)	C(31)-C(32)-C(33)	111.8(3)
C(22)-C(21)-C(25)	126.2(3)	C(34)-C(32)-C(33)	111.7(3)
O(2)-C(21)-C(25)	113.7(2)	C(31)-C(35)-C(37)	122.5(3)
C(21)-C(22)-C(23)	122.9(3)	C(31)-C(35)-C(36)	124.6(3)
C(21)-C(22)-C(24)	123.4(3)	C(37)-C(35)-C(36)	112.8(3)
C(23)-C(22)-C(24)	113.6(3)	C(51)-B(1)-C(41)	109.6(3)
C(21)-C(25)-C(27)	112.3(3)	C(51)-B(1)-C(61)	114.1(3)
C(21)-C(25)-C(26)	111.4(3)	C(41)-B(1)-C(61)	113.7(3)
C(27)-C(25)-C(26)	111.5(3)		
C(35)-C(31)-O(3)	120.9(3)		
C(35)-C(31)-C(32)	125.3(3)		

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z-1



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